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14. ABSTRACT JHU/APL's Polymer Claw is a pressure-activated underwater adhesive that bonds instantly to biofouled surfaces in a single step. The key to this technology is the use of pressure sensitive microcapsules, which release reactive amine crosslinkers into an adhesive putty when pressed against the surface. The amine reacts with the sticky, isocyanate putty to form a tough polyurea. The catalyzed isocyanates likewise bond with alcohols, amines, acids, or oxides on the surface. This technology addresses the issue of biofouling through an abrasive metal brush coated with a caustic gel. Activated by water, the caustic removes plant and animal matter before the adhesive even makes contact with the surface. Pressure from the adhesive putty flattens the metal bristles and displaces the gel to make way for the adhesive. The entire system will be sealed in disposable packaging for safe storage and transport. This aggressive approach meets the Navy's requirements for speed, robust performance in all conditions, and no special training.					
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POLYMER CLAW: INSTANT UNDERWATER ADHESIVE

Progress Report #1

Prepared for:

David K. Han
Office of Naval Research
Code 322
875 North Randolph Street
Arlington, VA 22203-1995

Prepared by:

Jason J. Benkoski, Ph.D., Senior Research Scientist
The Johns Hopkins University Applied Physics Laboratory
The Milton S. Eisenhower Research Center
11100 Johns Hopkins Rd, MS 21-N109
Laurel, MD 20723
Tel. (240) 228-5140

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1 Summary

After a kickoff meeting in February, we began initial experiments on the three main components of Polymer Claw: the pressure-triggered adhesive, the water-activated caustic, and the abrasive brush. We successfully synthesized amine-filled microcapsules and a dry mixture of caustic ingredients that only activate when hydrated. Initial work to modify metal brushes into a collapsible array of bristles was also successful.

2 Project Goals and Objectives

The first goal of the project is to synthesize amine-filled microcapsules and the adhesive putty matrix in the first two months of the program. Although both have essentially been achieved in the first month, we will spend the second month controlling the break strength, improving yields, and purification. No milestones are due until the end of month 5.

3 Key Accomplishments

3.1 Kickoff Meeting

A formal kickoff meeting including David Han, Jody Wood-Putnam, David Scheidt, and Jason Benkoski was held on February 10th at APL. This meeting gave APL the opportunity to explain the approach in more detail and receive feedback on the research plan. APL now has a better understanding of acceptance criteria for shear and tensile adhesion as a function of time, requirements for low temperature curing, the need to balance safety with the use of caustics, and the importance of proving the performance of individual components apart from the total adhesive system.

3.2 Amine Microencapsulation

The microencapsulation of amine-functional crosslinkers is much more challenging than encapsulating hydrophobic monomers or other oils. Because of their water solubility, compounds like diethylenetriamine (DETA) and polyethylenimine (PEI) must be encapsulated using a reverse-phase synthesis. In other words, they must be emulsified in a medium that is too hydrophobic for the amines to be soluble. (Microencapsulation is much easier in water.) DETA and PEI are also soluble in common organic solvents such as acetone and toluene. One must go to very nonpolar alkanes such as hexane or decalin just to ensure immiscibility.

Once the amines are suspended as droplets in an oily medium, the trick is to make sure that the diisocyanate crosslinker dissolves in the oil phase. Hexane, for example, will not dissolve either toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI)—two common isocyanate monomers. Only hexamethylenediisocyanate (HMDI) dissolves in hexane. Decalin, on the other hand, dissolves all three isocyanates but not DETA or PEI. A number of experiments showed that the combination of DETA, PEI, and HMDI would not form stable microcapsules.

Instead, the monomers simply polymerized into a bulk polymer phase that precipitated from the hexane.

We learned from our experiments that the viscosity of the hydrophobic medium needed to be relatively high to prevent the suspended DETA/PEI droplets from coalescing. We also found that even surfactants were insufficient to prevent coalescence. With guidance from the literature, we turned to hydrophobically modified nanoclays to stabilize the suspension. Nanoclays segregate to the oil/amine interface where they provide a protective coating. Since the dispersed nanoclay is much larger in dimension than a surfactant molecule, they provide greater spacing between adjacent droplets in the medium. This extra spacing is sufficient to prevent two droplets from merging when they make contact.

Figure 1 shows the experimental setup and some early results. Stable microcapsules can be formed using this approach, and we are currently working to purify them so that they can be easily added to an adhesive matrix of polyurea precursors.

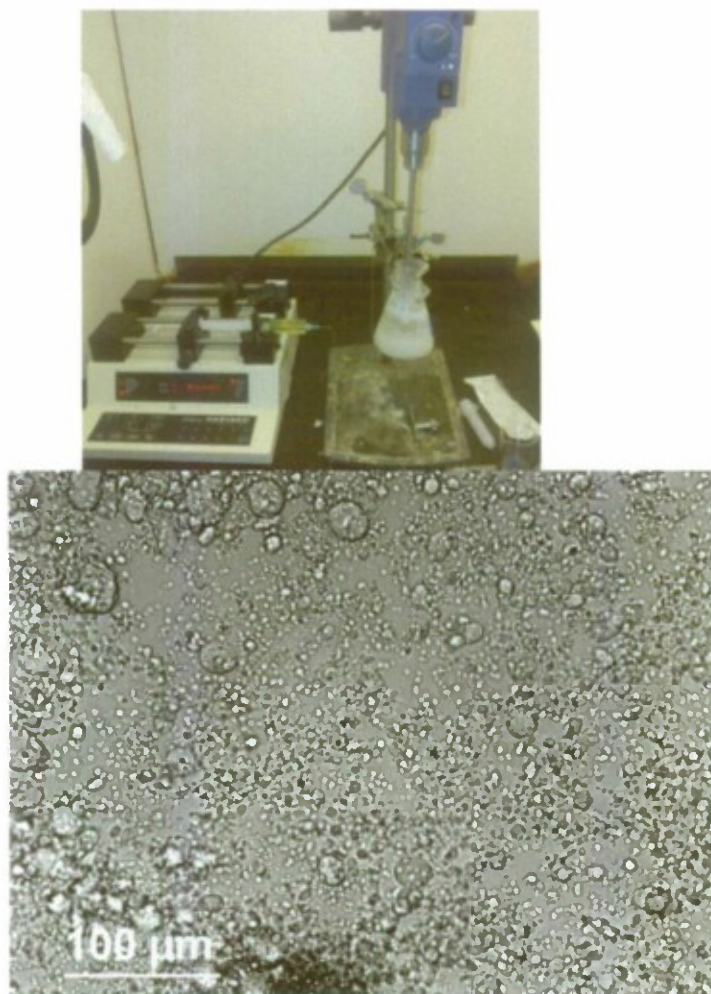


Figure 1: (left) Experimental setup for the formation of amine-filled microcapsules. The rapid polyurea reaction necessitated the use of a syringe pump for slow addition of reactants. (right) Example of amine-filled microcapsules consisting of 50% DETA and 50% PEI.

3.3 Caustic Cleaning Agent

In our proposal, we hypothesized that we could combine oxalic acid and sodium percarbonate to form an aggressive cleaning agent. The principle is that hydrogen peroxide combined with a strong acid would rapidly hydrolyze cellulosic matter such as algae or kelp. There are three major hurdles to this approach: (1) can oxalic acid and sodium percarbonate form a stable mixture, (2) can poly(acrylic acid) bind these ingredients to the ends of the metal brush, and (3) is the caustic mixture aggressive enough to break down cellulose.

We have already shown that the first two challenges are possible. Figure 2 shows a mixture of sodium percarbonate and oxalic acid in a plastic weigh boat. We have also been able to mix poly(acrylic acid) and surfactant powder with no reaction. So long as the ingredients remain dry, they do not react.

The second challenge was to use poly(acrylic acid) as a binder material to adhere the sodium percarbonate and oxalic acid powders to the tips of metal bristles. The process was easier than expected. Rather than having to melt the poly(acrylic acid), it was possible to moisten it with water, and then work in the two powders like a putty at room temperature. So long as the level of moisture was relatively low, the two active ingredients did not dissolve and set off the peroxide reaction.

The third challenge remains unanswered for now. Initial tests on paper show that a 1:1 mixture of oxalic acid and sodium percarbonate is insufficient to break down cellulose. A mixture of sodium percarbonate and sulfuric acid was, as expected, sufficiently aggressive to break down paper on contact.



Figure 2: (left) A stable powder of sodium percarbonate and oxalic acid next to a needle with the same attached to the end with poly acrylic acid. (center) Oxygen bubbles form immediately upon the addition of water, signifying the generation of peroxide radicals. (right) Even when using the poly(acrylic acid) binder, the generation of peroxide radicals is instantaneous.

3.4 Metal Brush

Both stainless steel and brass brushes have been purchased for evaluation. Initial tests show that pruning and bending the bristles should not be a problem.

4 Next Steps

4.1 Synthesis Improvements

Although it is possible to synthesize amine-filled microcapsules, we still have not demonstrated that they are sufficiently durable to be mixed with the adhesive putty without breaking. Further experiments must be done to control the polymer shell thickness by changing the reaction conditions. But before this can take place, we must develop a protocol for purifying the microcapsules from the excess nanoclay and polyisobutylene.

4.2 Caustic Improvements

Oxalic acid may not have a low enough pKa to effectively break down cellulose. Mineral acids cannot be used because they are liquids, and cannot form stable mixtures with sodium percarbonate. The key to having a water-activated caustic cleaning agent, is to start with dry powders. Fortunately, there are other options for acids that come in powder form. At least initially, we will explore the use of toluenesulfonic acid as a replacement for oxalic acid. Toluenesulfonic acid is similar in structure to sulfuric acid, except one oxygen is replaced by a benzene ring. It's pKa is -2.8, compared to 1.3 for oxalic acid and -3 for sulfuric acid.

Another key effort next month will be the development of a measurement to quantify the rate of cellulose hydrolysis. We will initially explore the possibility of measuring cellulose hydrolysis by monitoring the glucose concentration as a function of time (glucose is the byproduct of hydrolysis). Glucose concentration can be monitored using the dinitrosalicylate colorimetric method. Reference: Gail Lorenz Miller, Use of dinitrosalicylic acid reagent for determination of reducing sugar, *Analytical Chemistry*, **31**, 427, 1959.

4.3 Abrasive Brush

Work will begin next month to determine the critical load for collapsing the metal brush as a function of (1) bristle density, and (2) bristle angle. We will initially target a critical load of about 5 pounds (22 N), but knowing the two relationships above will allow us to modify it as needed.